



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 477 993 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

17.11.2004 Bulletin 2004/47

(51) Int Cl.7: H01B 1/12, H01B 1/20,

C08G 73/02, C08L 79/00,

C09D 5/24, C09D 7/12,

C09D 179/02, H05B 33/14,

H05B 33/26, H05B 33/28

(21) Application number: 03706965.5

(22) Date of filing: 19.02.2003

(86) International application number:

PCT/JP2003/001796

(87) International publication number:

WO 2003/071559 (28.06.2003 Gazette 2003/35)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT SE SI SK TR

Designated Extension States:

AL LT LV MK RO

(30) Priority: 20.02.2002 JP 2002043144

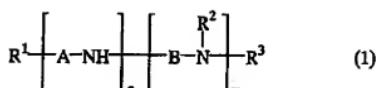
(71) Applicant: Nissan Chemical Industries, Ltd.
Chiyoda-ku, Tokyo 101-0054 (JP)

(72) Inventors:

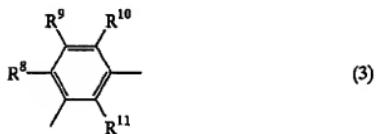
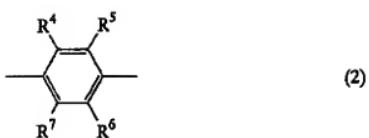
• YOSHIMOTO, Takuji,
Nissan Chemical Industries Ltd.,
Funabashi-shi, Chiba 274-8507 (JP)• FUKURO, Hiroyoshi,
Nissan Chemical Industries Ltd.
Funabashi-shi, Chiba 274-8507 (JP)• FURUSHO, Hitoshi,
Nissan Chemical Industries Ltd.
Tokyo 101-0054 (JP)• YANAGIMOTO, Akira,
Nissan Chemical Industries Ltd.
Tokyo 101-0054 (JP)(74) Representative: Stoner, Gerard Patrick
Mewburn Ellis LLP
York House
23 Kingsway
London WC2B 6HP (GB)

(54) ORGANIC CONDUCTIVE MATERIAL AND CONDUCTIVE VARNISH

(57) Disclosed herein are an organic conductive material and a conductive varnish containing it in an amount of 1 to 80 wt%. The organic conductive material comprises an oligoaniline derivative represented by the formula (1) in which quinolmine as an oxidant formed at the time of synthesis is reduced by a reducing agent and a salt is formed with an electron accepting dopant.



(where R^1 to R^3 independently denote a hydrogen atom, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, or acyl group; A and B independently denote a divalent group represented by the formula (2) or (3) below;



where, R^4 to R^{11} independently denote a hydrogen atom, hydroxyl group, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, acyl group, or sulfonyl group; and m and n independently denote a positive number equal to or larger than 1 such that $m+n \leq 20$.)

Description**TECHNICAL FIELD**

5 [0001] The present invention relates to an organic conductive material and a conductive varnish containing it. The organic conductive material is a salt of an oligoaniline derivative (which is a π -conjugated organic compound) with an acid and is highly soluble in water or organic solvents. The conductive varnish is a solution containing the organic conductive material dissolved or dispersed therein, which is capable of application by dip coating or spin coating. The conductive varnish containing the organic conductive material will be used to form organic conductive layers varying in thickness, such as a charge-injection auxiliary layer for organic electroluminescence (EL for short hereinafter) elements and an organic electrode on capacitor dielectrics or a capacitor electrode.

BACKGROUND ART

15 [0002] There has recently been proposed by Eastman Kodak a new organic EL element, particularly that of low molecular-weight type (OLED for short hereinafter), which realizes high luminance with a low driving voltage owing to its improved structure, with electrodes holding between them a charge transporting layer and an emitting layer formed by vapor deposition. (See Appl. Phys. Lett. 51 (1987) 913 and USP 4,356,429.) The ensuing active researches have led to the development of an element of three-layer type in which the emitting function is separated from the carrier transportation. Thus, the OLED element has entered the stage of practical use. (See Jpn. J. Appl. Phys. 27 (1988) L269, L713.) Moreover, a new EL element with a polymeric emitting material (PLED for short hereinafter) has been found in Cambridge College. (See Nature, 347 (1990), p. 539.) In addition, it has been found that the PLED has greatly improved characteristic properties if it is provided with a conductive organic material formed on the electrode. (See Appl. Phys. Lett. 64 (1994), p. 1245.) Now, such new PLED elements are comparable in characteristic properties to old OLED elements.

[0003] Conductive polymers are also finding use in the technology relating to capacitors. For example, a thin film of conductive polymer formed by electrolytic polymerization is gradually replacing manganese oxide interposed between the dielectric layer and the electrode for solution of problems with contact resistance.

20 [0004] Conductive polymers to be applied to such electronic devices are required to have a high solubility in solvents so that they provide a smooth thin film and infiltrate into minute gaps.

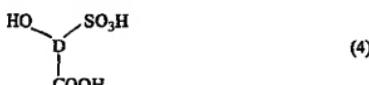
[0005] The present applicant invented a charge transporting varnish prepared from a low-molecular weight oligoaniline dissolved in an organic solvent and also found that this varnish gives rise to a hole injection layer which greatly improves the characteristic properties of EL elements. (See Japanese Patent Laid-open No. 2002-151272.)

25 [0006] Unfortunately, the aniline derivative has the quinolamine structure in its oxidized state, which remarkably impairs its solubility in solvents but contributes to its conductivity. For example, polyaniline polymerized by chemical oxidation has a very low solubility owing to its quinolamine structure. One way to increase solubility is to reduce the quinolamine structure with hydrazine. However, if a salt is formed by doping, the resulting product decreases in solubility. The problem with solubility remains unsolved.

DISCLOSURE OF INVENTION

30 [0007] It is an object of the present invention to provide an organic conductive material highly soluble in water and organic solvents and a conductive varnish containing it. It is another object of the present invention to provide an organic EL element made with the varnish.

35 [0008] In order to achieve the above-mentioned object, the present inventors carried out an extensive research, which led to the finding that an aniline oligomer in reduced form has an extremely high solubility if it is doped with an acid. For example, if an oligoaniline derivative in reduced form is doped with a sulfonic acid derivative represented by the formula (4)

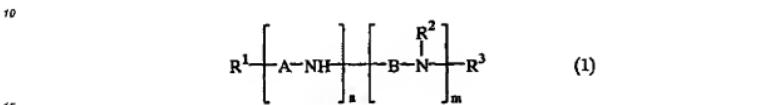


55

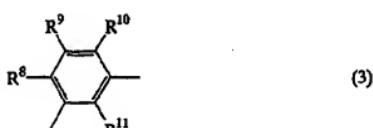
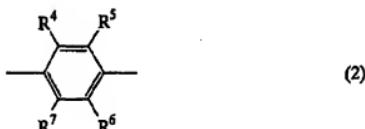
for salt formation, then the resulting salt is highly soluble in N,N-dimethylformamide, which is an organic solvent. A solution of this salt in N,N-dimethylformamide is useful as a conductive varnish which stably contains as much solids

(salt) as 70 wt%. Being poor in conductivity, the thin film formed from the varnish by spin coating or dip coating is oxidized by baking in the presence of oxygen so that the quinolimine structure is formed for improvement in conductivity. [0009] The present invention, which is based on the above-mentioned finding, provides an organic conductive material defined below, a conductive varnish containing it, a conductive thin film, and an organic EL element made with it.

5 [1] An organic conductive material which comprises an oligoaniline derivative represented by the formula (1) in which quinolimine as an oxidant formed at the time of synthesis is reduced by a reducing agent and a salt is formed with an electron accepting dopant.



(where R¹ to R³ independently denote a hydrogen atom, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, or acyl group; A and B independently denote a divalent group represented by the formula 20 (2) or (3) below;

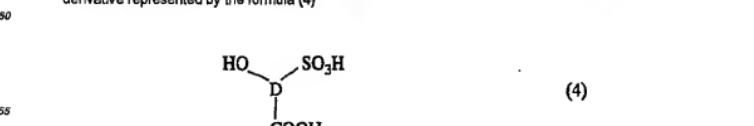


40 where, R⁴ to R¹¹ independently denote a hydrogen atom, hydroxyl group, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, acyl group, or sulfonic group; and m and n independently denote a positive number equal to or larger than 1 such that m+n≤20.)

45 [2] An organic conductive material as defined in [1] above, wherein R¹ and R² in the formula (1) denote a hydrogen atom, C₁₋₂₀ alkyl group, or C₁₋₂₀ alkoxy group.

[3] An organic conductive material as defined in [1] or [2] above, wherein R⁹ in the formula (1) denotes a hydrogen atom or aryl group.

[4] An organic conductive material as defined in any of [1] to [3] above, wherein the dopant is a sulfonic acid derivative represented by the formula (4)



(where D denotes a benzene ring, naphthalene ring, anthracene ring, phenanthrene ring, or heterocycle.)
 [5] A conductive varnish which comprises the organic conductive material defined in any of [1] to [4] defined above in an amount of 1 to 80 wt%.
 [6] A conductive thin film formed from the conductive varnish defined in [5] above.
 [7] An organic EL element having the conductive thin film defined in [6] above.

5

BRIEF DESCRIPTION OF DRAWINGS

[0010]

10

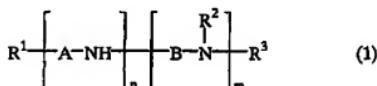
Fig. 1 is a confocal laser microphotograph ($\times 20$) of the coating surface obtained in Example 2.
 Fig. 2 is a confocal laser microphotograph ($\times 20$) of the coating surface obtained in Comparative Example 2.
 Fig. 3 is an optical microphotograph ($\times 50$) of the EL emitting surface obtained in Example 3. (What looks bright is the emitting surface.)
 15 Fig. 4 is an optical microphotograph ($\times 50$) of the EL emitting surface obtained in Comparative Example 4. (What looks bright is the emitting surface.)

BEST MODE FOR CARRYING OUT THE INVENTION

20

[0011] The organic conductive material according to the present invention is based on an oligoaniline derivative represented by the formula (1) below.

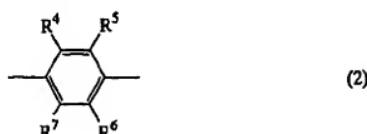
25



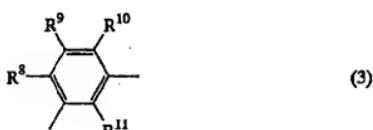
30

(where R^1 to R^3 independently denote a hydrogen atom, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, or acyl group; A and B independently denote a divalent group represented by the formula (2) or (3) below;

35



40



45

where R^4 to R^{11} independently denote a hydrogen atom, hydroxyl group, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, acyl group, or sulfonic group; and m and n independently denote a positive number equal to or larger than 1 such that $m+n \leq 20$.)

50

[0012] According to the present invention, the oligoaniline derivative represented by the formula (1) may be synthesized by any method without specific restrictions. A common method is by dehydration condensation reaction between

an aromatic amine and a phenol or by reaction between an aromatic amine and an aromatic amine hydrochloride in a molten state.

[0013] The oligoaniline derivative used in the present invention has substituents R¹ to R³, which independently denote a hydrogen atom, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, or acyl group.

[0014] The monovalent hydrocarbon group and organoxy group should preferably be those which have a carbon number of 1 to 20. The acyl group should preferably be those which have a carbon number of 2 to 20. Examples of the monovalent hydrocarbon group include alkyl groups (such as methyl group, ethyl group, propyl group, butyl group, t-butyl group, hexyl group, octyl group, and decyl group), cycloalkyl groups (such as cyclopentyl group and cyclohexyl group), bicycloalkyl groups (such as bicyclohexyl group), alkenyl groups (such as vinyl group, 1-propenyl group, 2-propenyl group, isopropenyl group, 1-methyl-2-propenyl group, 1- or 2- or 3-butenyl group, and hexenyl group), aryl groups (such as phenyl group, xylyl group, tolyl group, biphenyl group, and naphthyl group), and aralkyl groups (such as benzyl group, phenylethyl group, and phenylcyclohexyl group). These monovalent hydrocarbon groups may have their hydrogen atoms partly or entirely replaced by halogen atoms, hydroxyl groups, or alkoxy groups.

[0015] Examples of the organoxy group include alkoxy groups, alkenoxy groups, and aryloxy groups. The alkyl groups, alkenyl groups, and aryl groups in them are the same as those listed above.

[0016] The acyl group should preferably be the one which has a carbon number of 2 to 10. It includes, for example, acetyl group, propionyl group, butyryl group, isobutyryl group, and benzoyl group.

[0017] Preferred examples of R¹ and R² include a hydrogen atom, alkyl group or alkoxy group having a carbon number of 1 to 20, preferably 1 to 4, and phenyl group, cyclohexyl group, cyclopentyl group, biphenyl group, bicyclohexyl group, and phenylcyclohexyl group, which may have substituents, such as C₁₋₄ alkyl groups and alkoxy groups. Of these examples, alkyl groups, alkoxy groups, and C₂₋₄ acyl groups are particularly preferable. Preferred examples of R³ include a hydrogen atom and an aryl group (particularly a phenyl group).

[0018] The substituents R⁴ to R¹¹ are independently a hydrogen atom, hydroxyl group, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, acyl group, or sulfonic group. Preferred examples of the unsubstituted or substituted monovalent hydrocarbon group and organoxy group include those which have a carbon number of 1 to 20. Preferred examples of the acyl group include those which have a carbon number of 2 to 20. They are the same as those which are explained for R¹.

[0019] Preferred examples of the substituents R⁴ to R¹¹ include a hydrogen atom, alkyl group, alkoxy group, alkoxalkyl group, alkenyl group, acyl group, sulfonic group, and hydroxyl group. Additional examples include a phenyl group, cyclohexyl group, cyclopentyl group, biphenyl group, bicyclohexyl group, and phenylcyclohexyl group, each of which may have a C₁₋₄ alkyl group or alkoxy group as a substituent.

[0020] More preferred examples of R⁴ to R¹¹ include a hydrogen atom, C₁₋₂₀ alkyl group, C₁₋₂₀ alkoxy group, alkoxyalkyl group composed of C₁₋₂₀ alkoxy group and C₁₋₂₀ alkyl group, C₂₋₄ alkenyl group, C₂₋₄ acyl group, benzoyl group, sulfonic group, and hydroxyl group. Additional examples include a phenyl group, cyclohexyl group, biphenyl group, bicyclohexyl group, and phenylcyclohexyl group, each of which may have a C₁₋₄ alkyl group or C₁₋₄ alkoxy group as a substituent. Particularly preferred examples include a hydrogen atom, C₁₋₄ alkyl group, C₁₋₄ alkoxy group, alkoxyalkyl group composed of C₁₋₄ alkoxy group and C₁₋₄ alkyl group, vinyl group, 2-propenyl group, acetyl group, benzoyl group, sulfonic group, and hydroxyl group. Additional examples include a phenyl group, cyclohexyl group, biphenyl group, bicyclohexyl group, and phenylcyclohexyl group, each of which may have a C₁₋₄ alkyl group or C₁₋₄ alkoxy group as a substituent.

[0021] The subscripts m and n for the oligoaniline unit are independently a positive number of 1 or above. The sum of m+n should preferably be no larger than 20 for good solubility in solvents. It should be no larger than 10, particularly no larger than 5, if the vanish is to have a concentration equal to or higher than 20 wt%.

[0022] According to the present invention, the oligoaniline derivative prepared as mentioned above contains quinolmine as an oxidant which is formed at the time of synthesis, and this quinolmine is reduced by a reducing agent.

[0023] In other words, the aniline oligomer which has been synthesized is washed with organic solvents (such as toluene and ether sequentially) and then dried to give silvery crystals. The crystals undergo reduction as follows for improvement in solubility. The procedure for reduction is not specifically restricted. The crystals are dissolved in an organic solvent (such as dioxane which is compatible with the crystals), and the resulting solution is given a reducing agent, such as hydrazine. With the atmosphere in the reaction system replaced by an inert gas such as nitrogen, the crystals are dissolved with heating under refluxing. The resulting solution is given an organic solvent (such as toluene which is incompatible with the crystals) for precipitation. The precipitates are dissolved in an organic solvent (such as dioxane which is compatible with the crystals) with heating under refluxing, and the resulting solution is filtered. The filtrate is allowed to separate solids, and the separated solids are recrystallized. In this way, there is obtained the desired oligoaniline derivative (in the form of white crystals) to be used in the present invention.

[0024] The reducing agent used for reduction mentioned above is hydrazine or the like. It should be used in an amount of 0.1-10 parts by weight, particularly 0.5-2 parts by weight, for 100 parts by weight of the oligoaniline derivative to be purified. Examples of the compatible organic solvents include dioxane, tetrahydrofuran, N,N-dimethylformamide,

N,N-dimethylacetamide, and N-methylpyrrolidone. Examples of the incompatible organic solvents include toluene, ether, xylene, benzene, chlorobenzene, dichlorobenzene, dichloromethane, dichloroethane, chloroform, hexane, and heptane.

[0025] According to the present invention, the oligoaniline derivative represented by the formula (1) shown above is obtained by the procedure mentioned above. Subsequently, a salt is formed by reaction with an electron accepting dopant. The acid which forms a dope (salt) with the dopant should preferably be a sulfonic acid derivative represented by the formula (4)

10



15

(where D denotes a benzene ring, naphthalene ring, anthracene ring, phenanthrene ring, or heterocycle) which easily brings about intermolecular mutual reactions. Examples of the dopant include sulfoalicylic acid derivatives. The dopant should be added in such an amount that the number of dopant molecules is no more than one, preferably 0.2 to 1, for one nitrogen atom in the oligoaniline derivative, depending on the molecular weight of the oligoaniline derivative.

[0026] The oligoaniline derivative is dissolved in a solvent to give the varnish. The solvent used for this purpose is not specifically restricted so long as it dissolves the oligoaniline derivative. Examples of the solvent include water and organic solvents (such as N-methylpyrrolidone, N,N-dimethylacetamide, and N,N-dimethylformamide). These solvents may be used alone or in combination with one another.

[0027] The dopant may be added in any manner which is not specifically restricted. One procedure may consist of the following steps. The oligoaniline derivative is added to a solvent (such as DMF) under a stream of inert gas (such as nitrogen) for complete dissolution. The dopant is dissolved in a solvent (such as DMF). The amount of the dopant is determined according to the specific molar ratio of the dopant to the amount of nitrogen atoms contained in the oligoaniline derivative. The solution of the dopant is slowly added to the solution of the oligoaniline derivative. In this way there is readily obtained a solution of doped oligoaniline. Doping may be accelerated by heating.

[0028] The above-mentioned solvent capable of uniformly dissolving the oligoaniline derivative may be mixed with a solvent which hardly dissolves the oligoaniline derivative when used alone. Examples of such a solvent include ethyl cellulose, butyl cellosolve, ethylcarbitol, butyl carbitol, ethylcarbitol acetate, and ethylene glycol.

[0029] Incidentally, the concentration of the oligoaniline derivative in the solution may be adjusted within the range of 1-80 wt%, particularly 1-50 wt%.

[0030] It is possible to form a thin film of the oligoaniline derivative on a substrate by applying the solution of the oligoaniline derivative onto a substrate and heating the coated solution to evaporate the solvent. The heating temperature is usually 80-200°C, which is high enough for solvent evaporation.

[0031] Coating form the thin film of the oligoaniline derivative is accomplished by dip coating, spin coating, transfer printing, roll coating, or brushing.

[0032] Incidentally, the thus obtained thin film should be thoroughly baked in the presence of oxygen so as to form the quinolimine structure which contributes to improved conductivity.

[0033] The conductive thin film to be obtained by coating and ensuing evaporation is not specifically restricted in thickness. However, a thickness ranging from 5 to 200 nm is desirable in the case where the thin film is used as the charge injection layer in an organic EL element. The film thickness may be varied by adjusting the concentration of solids in the varnish or by adjusting the amount of the varnish to be applied to the substrate.

[0034] The following method and material may be used to form OLED elements with the conductive varnish of the present invention, although they are not limitative.

[0035] The first step is to clean the electrode substrates with detergent, alcohol, pure water, etc. The cleaned anode substrate should preferably undergo surface treatment (such as ozone treatment and oxygen-plasma treatment) immediately before its use. However, this surface treatment may be omitted if the anode substrate is composed mainly of organic substances.

[0036] The following method is suitable for production of an OLED element with the conductive varnish.

[0037] First, the conductive varnish is applied to the anode substrate to form a conductive thin film thereon. Then, the coated anode substrate is placed in a vacuum vapor deposition apparatus, and vapor deposition is carried out to form thereon sequentially a hole transport layer, an emitting layer, an electron transport layer, an electron injection layer, and a cathode metal. A carrier block layer may be formed optionally between any adjacent layers to control the

emitting region. Thus there is obtained a desired OLED element.

[0038] The anode may be formed from a transparent electrode material, such as indium tin oxide (ITO) and indium zinc oxide (IZO), which should preferably be planarized. It may also be formed from a polythiophene derivative or polyaniline highly capable of charge transportation.

5 [0039] The hole transporting layer may be formed from any of the following compounds.

- triarylamine, such as (triphenylamine) dimer derivative (TPD), (α -naphthylidiphenylamine) dimer (α -NPD), and [(triphenylamine) dimer] spirodimer (Spiro-TAD).
- "Starburstamine", such as 4,4',4"-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) and 4,4',4"-tris [m-phenyl(phenyl)amino]triphenylamine (1-TNATA).
- oligothiophene, such as 5,5'-bis[4-(bis[4-methylphenyl]-amino)phenyl]-2,2',5,2"-terthiophene (BMA-37).

[0040] The emitting layer may be formed from any of (8-quinolinolato) aluminum (III) (Alq_3), bis(8-quinolinolato) zinc (II) (Znq_2), bis(2-methyl-8-quinolinolato)(p-phenylphenolate) aluminum (II) ($BAIq$), and 4,4'-bis(2,2-diphenylvinyl) biphenyl (DPVBi). The emitting layer may be formed by codeposition of the electron transporting material (or hole transporting material) and the emitting dopant.

15 [0041] Examples of the electron transporting material include Alq_3 , $BAIq$, DPVBi, (2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) (PBD), triazole derivative (TAZ), bathocuproine (BCP), and silole derivative.

20 [0042] Examples of the emitting dopant include quinacridone, rubrene, coumarin 540, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), tri(2-phenylpyridine) Iridium (III) ($Ir(ppy)_3$), and (1,10-phenanthroline)-tris(4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate) europium (III) ($Eu(TTA)_3phen$).

[0043] The carrier blocking layer may be formed from any of PBD, TAZ, BCP, etc.

[0044] The electron injection layer may be formed from any of lithium oxide (Li_2O), magnesium oxide (MgO), alumina (Al_2O_3), lithium fluoride (LiF), magnesium fluoride (MgF_2), strontium fluoride (SrF_2), Li_3 , Li , $Li(acac)$, lithium acetate, lithium benzoate, etc.

[0045] The cathode may be formed from any of aluminum, magnesium-silver alloy, aluminum-lithium alloy, lithium, sodium, potassium, cesium, etc.

[0046] No specific restrictions are imposed on the method of preparing the PLED element with the charge transporting varnish of the present Invention. Some examples of the method are shown below.

30 [0047] The PLED element containing the conductive thin film, which is formed from the conductive varnish of the present Invention, may be obtained by forming the polymeric layer for emission and charge transportation, in place of vacuum deposition to form the hole transporting layer, emitting layer, electron transporting layer, and electron injection layer in production of the OLED element mentioned above. To be concrete, the conductive thin film is formed on the anode substrate from the conductive varnish by the above-mentioned method. Then, the polymeric layer for emission and charge transportation is formed on it. Finally, the cathode is formed by vapor deposition. In this way there is obtained the PLED element.

35 [0048] The polymeric layer for emission and charge transportation is formed in the following manner. The polymeric material for emission and charge transportation alone or together with the emission dopant is uniformly dissolved or dispersed in a solvent. The resulting solution is applied to the electrode substrate on which the conductive thin film has been formed. Finally, the thin film is obtained after solvent evaporation.

40 [0049] Examples of the polymer for emission and charge transportation include polyfluorene derivative, such as poly(9,9-dialkylfluorene) (PDAF), polyphenylenevinylene derivative, such as poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV), polythiophene derivative, such as poly(3-alkylthiophene) (PAT), and polyvinylcarbazole (PVCar).

45 [0050] Examples of the solvent include toluene, xylene, and chloroform. Dissolution or dispersion may be accomplished by stirring, stirring with heating, or ultrasonic dispersion.

[0051] The method for coating is not specifically restricted. Coating may be accomplished by dip coating, spin coating, transfer printing, roll coating, or brushing. Coating should preferably be accomplished under a stream of inert gas such as nitrogen and argon.

50 [0052] Solvent evaporation may be accomplished by heating with an oven or hot plate under an inert gas stream or in a vacuum.

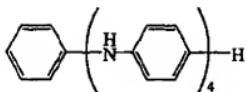
EXAMPLES

55 [0053] The Invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope thereof.

Example 1

[Preparation of phenyltetraaniline varnish]

5 [0054]



15 [0055] In 2 liters of toluene was dissolved 12.977 g of p-phenylenediamine. In the resulting solution was dissolved 245.05 g of tetra-*n*-butoxy titanium (which is a dehydration condensing agent) at 70°C over 30 minutes. To the solution was added 53.346 g of p-hydroxydiphenylamine, and the solution was heated at 100°C for 24 hours under a nitrogen atmosphere. After the reaction was complete, the reaction mixture was filtered and separated solids were washed sequentially with toluene and ether and finally dried. Thus there were obtained silvery crystals. The crystals, together with 0.2 mol of hydrazine monohydrate, were dissolved in as much dioxane as 25 times the weight of the crystals, by heating with refluxing, with the atmosphere in the reaction system replaced by nitrogen. To the resulting solution was added as much toluene as 25 times the weight of the crystals, so that the solution was suspended in toluene. The resulting suspension was heated with refluxing. As much dioxane as 10 times the weight of the crystals was added, and the crystals were dissolved by heating with refluxing. The resulting solution was filtered while it was still hot. The solids which had separated out from the filtrate were recrystallized, and the resulting crystals were washed sequentially with toluene-dioxane (1:1) and ether under a nitrogen atmosphere. The crystals were filtered off and dried at 60°C for 10 hours under reduced pressure. The procedure for recrystallization was repeated again. Thus, there was obtained 38.80 g of white crystals. (yield: 75%)

20 [0056] The thus obtained white crystals were doped with 5-sulfosalicylic acid (as a dopant) under the condition shown in Table 1. The resulting product was dissolved in DMF to give the desired varnish.

25

Table 1

(Conditions for preparation of varnish)					
	Run No.	Phenyltetraaniline (g)	Dopant (g)	Solvent DMF (g)	Concentration (wt%)
35	1	1.00	0.574	29.91	5
40	2	1.00	1.148	40.81	5
45	3	1.00	1.723	51.74	5
	4	1.00	2.297	62.64	5
	5	7.50	17.23	89.16	20
	6	15.0	34.47	66.87	40
	7	15.0	34.47	21.20	70

50 [0057] The samples of conductive varnish shown in Table 1 remained stable during storage at 0°C for 3 months under an atmosphere of nitrogen. The storage stability was proved by the fact that no aggregates were found after filtration.

[0058] The conductive varnish (8 g) designated as Run No. 4 in Table 1 was tested for time required to pass through a PTFE membrane filter, 25 mm in diameter, having a pore diameter of 0.2 µm. The results are shown in Table 2.

Comparative Example 1

55 [0059] A sample of conductive varnish (5 wt% concentration) was prepared under the same conditions as the conductive varnish designated as Run No. 4 in Table 1, except that the phenyltetraaniline was not reduced. This sample was tested for time required to pass through a PTFE membrane filter in the same way as in Example 1. The results

are shown in Table 2.

Table 2

(Time required for passage through a filter)	
	Time for passage
Example 1	15 seconds
Comparative Example 1	62 seconds

[0060] It is apparent from Table 2 that the 5 wt% varnish without reduction in Comparative Example 1 contains undissolved particles.

Example 2

[0061] The conductive varnish designated as Run No. 4 in Table 1 was applied by spin coating to an ITO glass substrate which had undergone ozone cleaning for 40 minutes. The coated substrate was baked at 180°C for 2 hours on a hot plate. Thus there was obtained a conductive thin film, 40 nm thick. The conductive thin film was observed under a confocal laser microscope, whose microphotograph is shown in Fig. 1.

Comparative Example 2

[0062] A conductive thin film (40 nm thick) was obtained by the procedure mentioned in Example 2 from the varnish prepared by the procedure mentioned in Comparative Example 1. The conductive thin film was observed under a confocal laser microscope, whose microphotograph is shown in Fig. 2. Comparison between Fig. 1 and Fig. 2 indicates that the coating film is uneven due to undissolved particles.

Example 3

[0063] The conductive varnish designated as Run No. 4 in Table 1 was applied by spin coating to an ITO glass substrate which had undergone ozone cleaning for 40 minutes. The coated substrate was baked at 180°C for 2 hours on a hot plate so as to form a hole injection layer (20 nm thick). The substrate was placed in a vacuum deposition apparatus, and vapor deposition was performed to form four layers sequentially as follows.

- 35 • (α-naphthylidiphenylamine)dimer (α-NPD), 40 nm thick.
- tris(β-quinololinate aluminum (III)) (Alq₃), 60 nm thick.
- LiF, 0.5 nm thick.
- Al, 100 nm thick.

40 Vapor deposition for each layer was carried out at a pressure no higher than 8×10⁻⁴ Pa. The rate of deposition was 0.3-0.4 nm/s (except for the LiF layer). The rate of deposition for the LiF layer was 0.02-0.04 nm/s. The substrate was transferred in a vacuum from one step to another. The thus obtained organic electroluminescence element has the characteristic properties as shown in Table 3. The photograph of the emitting surface is shown in Fig. 3.

Comparative Example 3

[0064] An organic EL element was prepared under the same conditions as in Example 3 from the conductive varnish mentioned in Comparative Example 1. The resulting organic EL element has the characteristic properties as shown in Table 3. The photograph of the emitting surface is shown in Fig. 4. It is apparent from Table 3 that the organic EL element according to the present invention has good characteristic properties. Comparison between Fig. 3 and Fig. 4 indicates that the organic EL element according to the present invention has a uniform emitting surface (Fig. 3).

Table 3

(Characteristic properties of organic EL elements)		Voltage (V)	Current density (mA/cm ²)	Luminance (cd/m ²)	Current efficiency (cd/A)
5	Example 3	8.0	0.090	28.6	3.92
10	Example 3	10.0	0.729	199.1	4.20
15	Comparative Example 3	8.0	2.32	1.0	1.11
20	Comparative Example 3	10.0	4.74	95.3	4.11

Example 4

[Preparation of phenylpentaaniline varnish]

[0065] 4,4'-diaminodiphenylamine (DADPA) was obtained from 4,4'-diaminodiphenylamine sulfate by recrystallization (for desalting) in an excess aqueous solution of sodium hydroxide. The thus obtained DADPA was reacted and purified in the same way as in Example 1 to give phenylpentaaniline. The phenylpentaaniline was dissolved in DMF and then doped with sulfosalicylic acid. Table 4 shows the amount of doping and the conditions for preparation of varnish.

Table 4

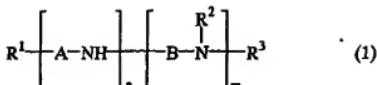
(Conditions for preparation of varnish)					
Run No.	Phenylpentaaniline (g)	Dopant (g)	Solvent DMF (g)	Concentration (wt%)	
25	1	1.00	0.476	28.04	5
30	2	1.00	1.953	37.11	5
35	3	1.00	2.429	46.15	5
40	4	1.00	2.905	55.20	5
45	5	1.00	3.381	64.24	5
50	6	1.00	3.381	17.52	20
55	7	1.00	3.381	6.57	40

[0066] The samples of conductive varnish shown in Table 4 remained stable during storage at 0°C for 3 months under an atmosphere of nitrogen. The storage stability was proved by the fact that no aggregates were found in the filtration test carried out in the same way as in Example 1.

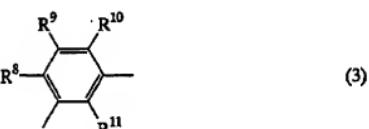
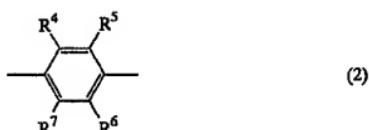
[0067] As shown in Examples mentioned above, the oligoaniline derivative according to the present invention is easy to synthesize, and it can be used as one of the raw materials to give a coating film having good heat resistance, high strength, good film properties, good antistatic properties, and weak tendency toward charge accumulation. The oligoaniline derivative in reduced form is readily soluble, and hence it is useful to give a conductive varnish heavily containing the organic conductive material of the present invention in which the oligoaniline derivative is used as a dopant. The conductive varnish can be used to form the charge injection auxiliary layer of the organic EL element, the organic electrode on a dielectric material of a capacitor, and the capacitor electrode, which broadly vary in thickness.

Claims

1. An organic conductive material which comprises an oligoaniline derivative represented by the formula (1) in which quinolmine as an oxidant formed at the time of synthesis is reduced by a reducing agent and a salt is formed with an electron accepting dopant.



10 (where R^1 to R^3 independently denote a hydrogen atom, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, or acyl group; A and B independently denote a divalent group represented by the formula (2) or (3) below;



25 where, R^4 to R^{11} independently denote a hydrogen atom, hydroxyl group, unsubstituted or substituted monovalent hydrocarbon group, organoxy group, acyl group, or sulfonic group; and m and n independently denote a positive number equal to or larger than 1 such that $m+n \leq 20$.)

30

2. The organic conductive material as defined in Claim 1, wherein R^1 and R^2 in the formula (1) denote a hydrogen atom, C_{1-20} alkyl group, or C_{1-20} alkoxy group.
- 40 3. The organic conductive material as defined in Claim 1 or 2, wherein R^3 in the formula (1) denotes a hydrogen atom or acyl group.
4. The organic conductive material as defined in any of Claims 1 to 3, wherein the dopant is a sulfonic acid derivative represented by the formula (4)

45



50

(where D denotes a benzene ring, naphthalene ring, anthracene ring, phenanthrene ring, or heterocycle.)

55

5. A conductive varnish which comprises the organic conductive material defined in any of Claims 1 to 4 in an amount of 1 to 80 wt%.
6. A conductive thin film formed from the conductive varnish defined in Claim 5.

7. An organic electroluminescence element having the conductive thin film defined in Claim 6.

5

10

15

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/01796

A. CLASSIFICATION OF SUBJECT MATTER	
Int.Cl ⁷ H01B1/12, 1/20, C08G73/02, C08L79/00, C09D5/24, 7/12, 179/02, H05B33/14, 33/26, 33/28	

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)	
Int.Cl ⁷ H01B1/12, 1/20, C08G73/02, C08L79/00, C09D5/24, 7/12, 179/02, H05B33/14, 33/26, 33/28	

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:
Jitsuyo Shinan Kobo 1926-1996 Tokuju Jitsuyo Shinan Kobo 1994-2003
Kokai Jitsuyo Shinan Kobo 1971-2003 Jitsuyo Shinan Tokuju Kobo 1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-506497 A (International Business Machines Corp.), 08 June, 1999 (08.06.99), Full text & WO 98/5043 A1	6 US 6099756 A 1-3
Y		5-7
A		4
X	JP 11-504982 A (International Business Machines Corp.), 11 May, 1999 (11.05.99), Full text & WO 98/5044 A1	6 US 6140462 A 1-3
Y		5-7
A		4
Y	JP 11-195491 A (Pioneer Electronic Corp.), 21 July, 1999 (21.07.99), Claims; Par. Nos. [0023] to [0026] & US 2001/0011867 A1	5-7

 Further documents are listed in the continuation of Box C. See parent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document published on or after the international filing date which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)
- "C" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered new or cannot be distinguished as involving an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search 27 May, 2003 (27.05.03)	Date of mailing of the international search report 24 June, 2003 (24.06.03)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/01796

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2001-160493 A (Junji KIDO et al.), 12 June, 2001 (12.06.01), Full text	5-7
A	6 WO 01/41513 A1 6 EP 1248497 A1 6 US 2002/0197494 A1	1-4
A	JP 11-322923 A (Japan Science and Technology Corp.), 26 November, 1999 (26.11.99), (Family: none)	4
A	JP 9-227675 A (Nitto Denko Corp.), 02 September, 1997 (02.09.97), (Family: none)	1-7
A	JP 3-111425 A (Kabushiki Kaisha Tomoekawa Seisakusho), 13 May, 1991 (13.05.91), (Family: none)	1-7
P,A	JP 2002-151272 A (Nissan Chemical Industries, Ltd.), 24 May, 2002 (24.05.02), (Family: none)	1-7